Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 282-284

In situ growth of four MOF/LZH composites on layered zinc hydroxide and their photocatalytic performance in decomposition of organic dyes

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1. General procedure for the preparation of layered Zn hydroxide (LZH):

In a typical experiment, $Zn(NO_3)_2$ (5 mmol) was dissolved in deionized H_2O (25 ml) to give a clear solution after stirring for 5 min. Then triethanolamine (1 ml) was slowly added under stirring. The resulting mixture was placed in a Teflon-lined stainless steel vessel and kept in an oven at 110 °C for 2 h. After that, it was cooled down to room temperature, and solid products at the bottom of autoclave were washed with deionized H_2O several times and dried at 60 °C for 24 h.

2. Preparation of MOF/LZH composite

MOF/LZH composite were synthesized using LZH as the Zn^{2+} precursor *via* the modified hydro-thermal method developed by Belén Fernández group. The prepared LZH (5 mmol) was dissolved in a DMF/H_2O(deionized) mixture (25 ml, 1 : 2 by vol.) and stirred for 5 min. Then, bi-phenyl-4,4'-dicarboxylic acid (5 mmol) was slowly added under stirring. The resulting mixture was placed in a Teflon-lined stainless steel vessel and kept in an oven at 120 °C for 2 h. It was cooled down to room temperature, and solid products at the bottom of autoclave were washed with deionized H_2O several times and dried at 60 °C for 24 h. A series of MOF/LZH composite photocatalysts was obtained varying the time of synthesis (2, 4, 6 and 8 h), and named as MOF/LZH-2, MOF/LZH-4, MOF/LZH-6 and MOF/LZH-8, respectively.

3. Characterization methods

LZH samples was characterized by the SEM, Powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) surface measurements, and thermogravimetric analysis (TGA). XRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.5408$ Å) at 40 kV and 30 mA current. FTIR spectrum was recorded in the range of 400-4000 cm^{-1} on a Nicolet (Impact 410) spectrometer in KBr pellets at room temperature. The surface morphology was accomplished by SEM using Vega 3 Tescan at the acceleration voltage of 20.0 kV. The BET surface was determined *via* N_2 adsorption-desorption at 77 K using a Micromeritics ASAP 2000 instrument. TGA analysis was performed on a Perkin-Elmer thermogravimetric analyzer

Pyris 1 TGA up to 1023 K at the heating rate of 10 K min^{-1} under N_2 atmosphere. Solid-state UV–Vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 double monochromator spectrophotometer using $BaSO_4$ as a standard of the 100% reflectance.

4. Photocatalytic activity testing

The catalytic activity of MOF/LZH composites was evaluated by the degradation of methyl orange dye using a photocatalytic reactor (UV irradiation at $\lambda = 365$ nm) at room temperature. Firstly, the mixture was magnetically stirred in the dark for 1 h in order to ensure reaching the equilibrium between adsorption and desorption. The mixture solution was then exposed under UV irradiation for certain amount. Next, the MOF/LZH composites were separated from the solution by a centrifugation. Last, the concentration of dye at equilibrium was detected at 401 nm by UV–Vis spectrophotometer for monitoring of the photocatalytic degradation process.

5. The procedure for the detection of super oxide anion radicals

The mixed solution of MOF/LZH composite and water was exposed to UV irradiation for a certain time. Next, the mixed solution (1 ml) was fractioned by centrifugation, the supernatant was discarded, a blue precipitate was collected and treated with KOH (45%, 2 mol dm^{-3}) and DMSO (55%). The precipitate was dissolved, centrifuged again, and tested for the reducing ability towards the supernatant product by absorbance at 680 nm.

6. The procedure for the detection of OH radicals

The mixed solution of MOF/LZH composite, terephthalic acid, and NaOH was exposed o UV irradiation for a certain time. Next, the mixed solution (1 ml) was fractioned by centrifugation. Then, the fluorescence intensity of clear solution was measured in order to detect the formation of hydroxyl groups as quenching the fluorescent effect of terephthalic acid by hydroxyl radicals.

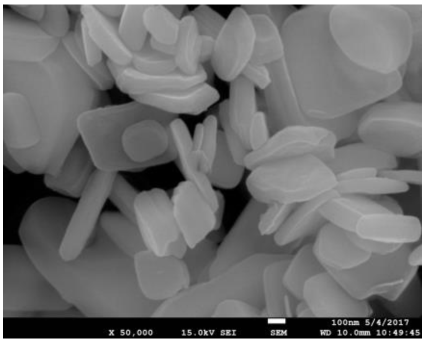

Figure S1 (*a*) SEM images of LZH–NO_3.

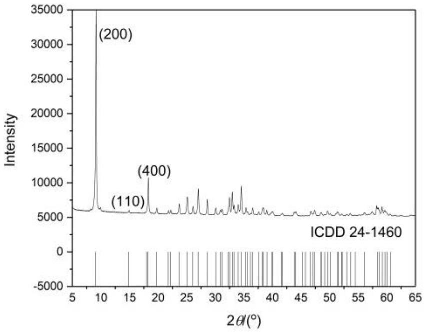

Figure S1 (*b*) XRD patterns of LZH–NO_3.

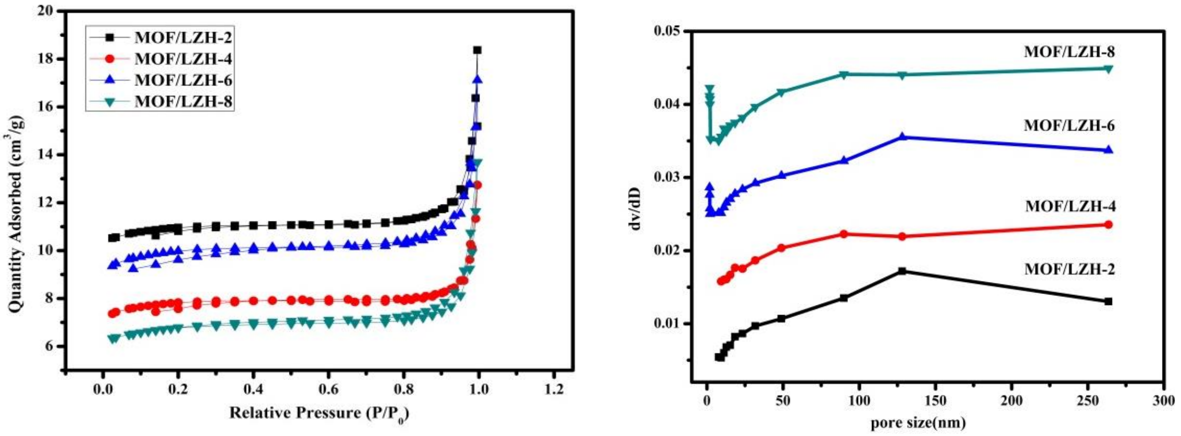

Figure S2 (*a*, left) Nitrogen sorption isotherms and pore size distribution (*b*, left) for the four MOF/LZH composites.

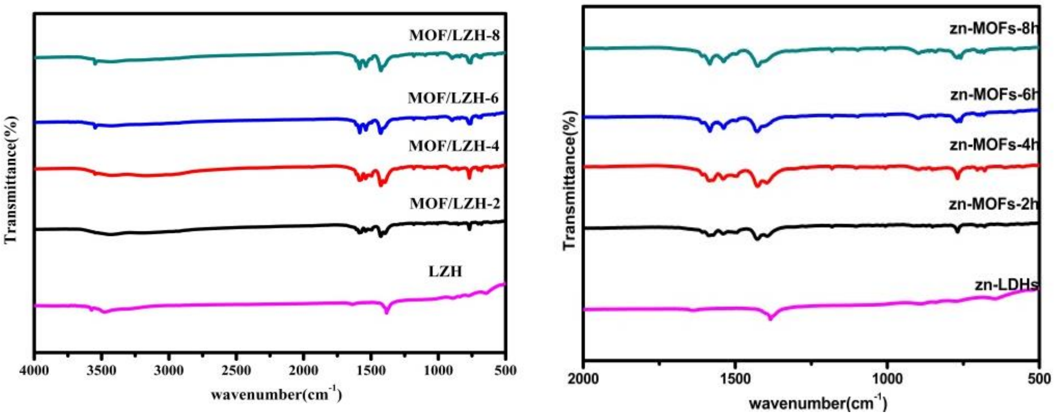

Figure S3 FTIR spectra of four MOF/LZH composites and pure LZH in the ranges of (right) 4000–400 and (left) 2000–400 cm^{-1}.

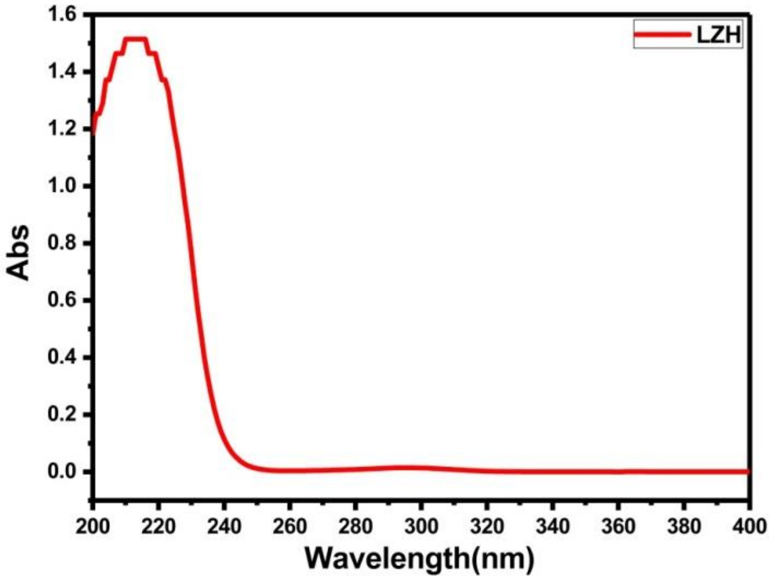

Figure S4 UV−DRS for pure LZH.

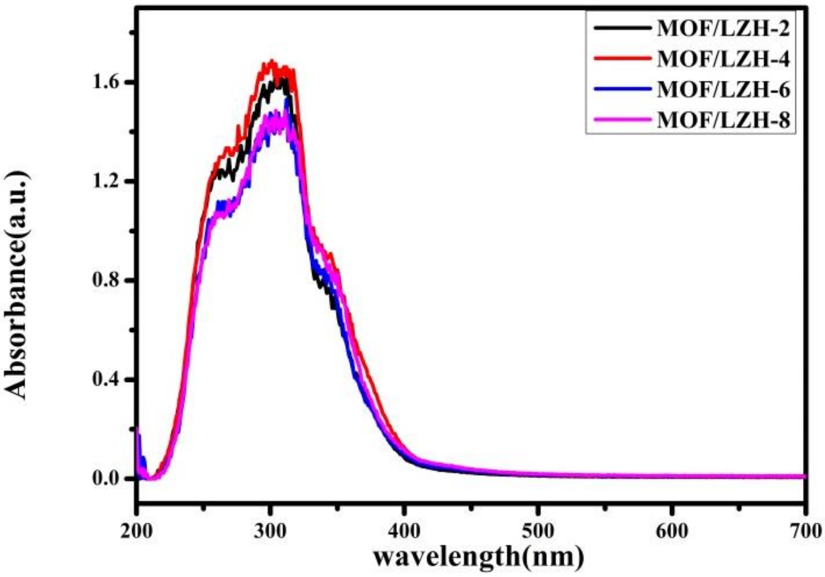

Figure S5 The UV−Vis diffuse reflectance spectra of the obtained MOF/LZH composites.

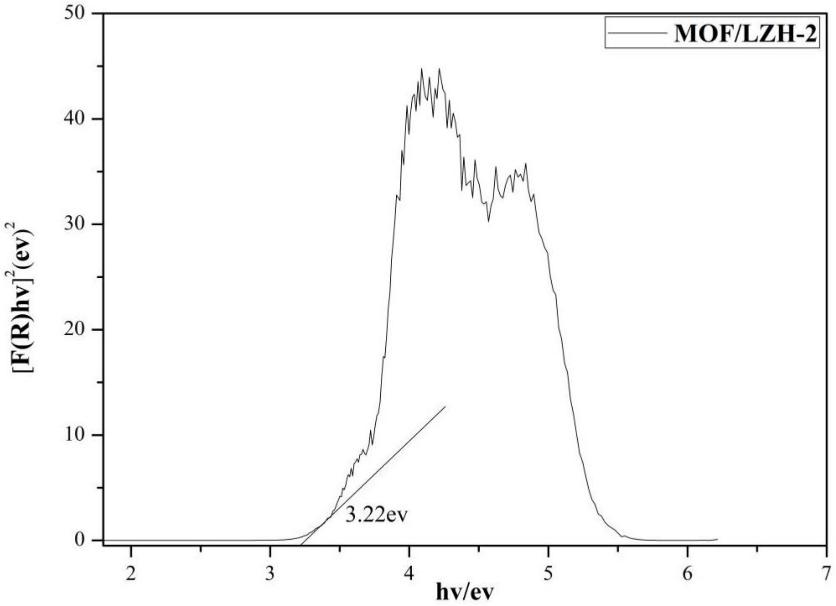

Figure S6 UV–DRS and E_g values for MOF/LZH-2 composite.

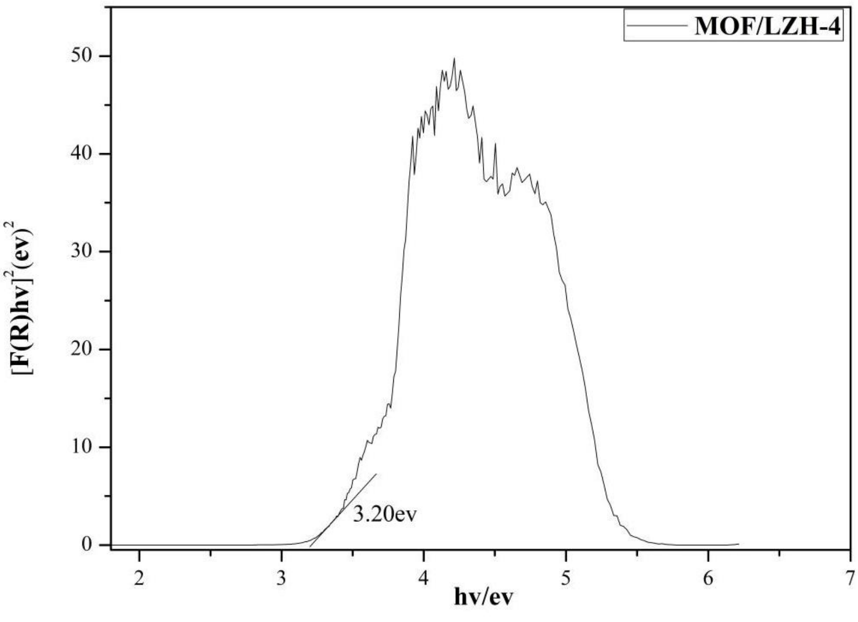

Figure S7 UV–DRS and E_g values for MOF/LZH-4 composite.

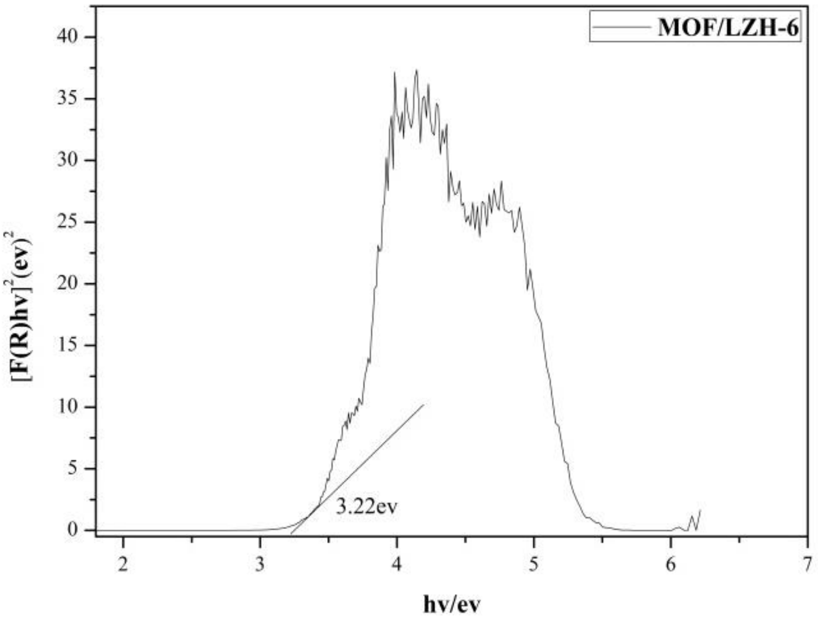

Figure S8 UV–DRS and E_g values for MOF/LZH-6 composite.

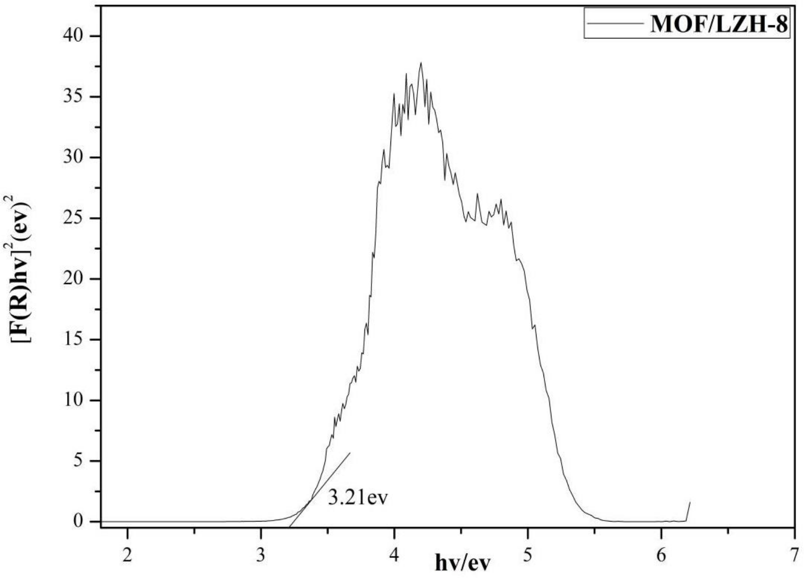

Figure S9 UV–DRS and E_g values for MOF/LZH-8 composite.

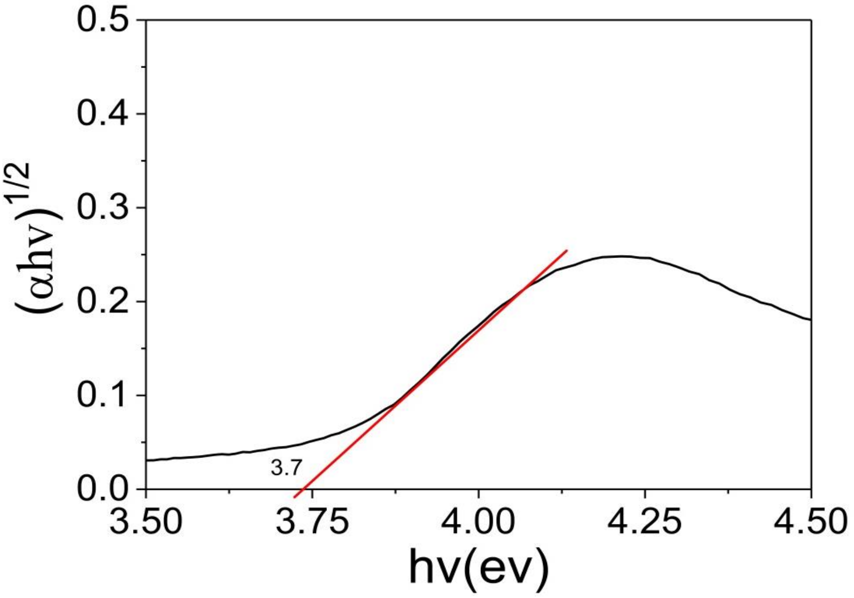

Figure S10 UV–DRS and E_g values for pure LZH.

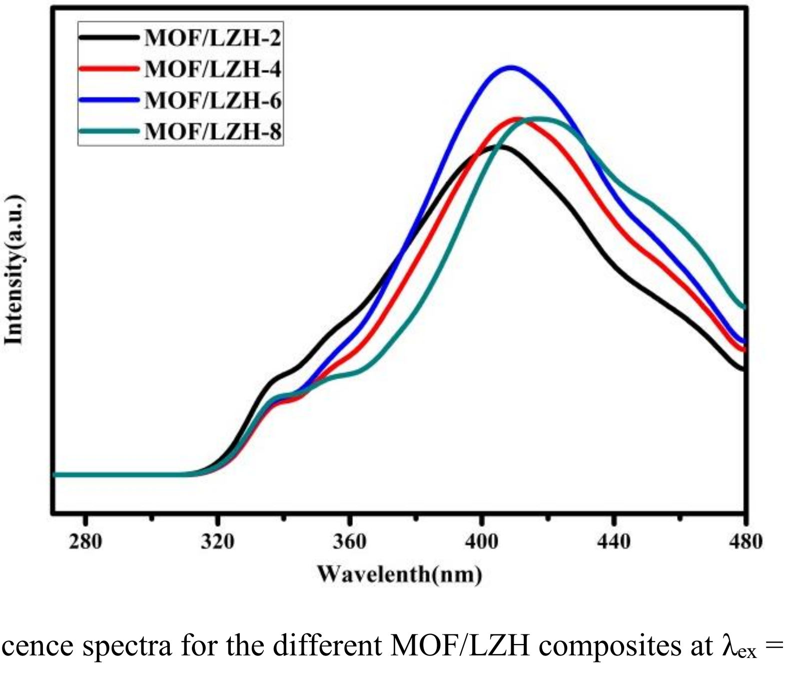

Figure S11 Fluorescence spectra for the different MOF/LZH composites at λ_{ex} = 240 nm.

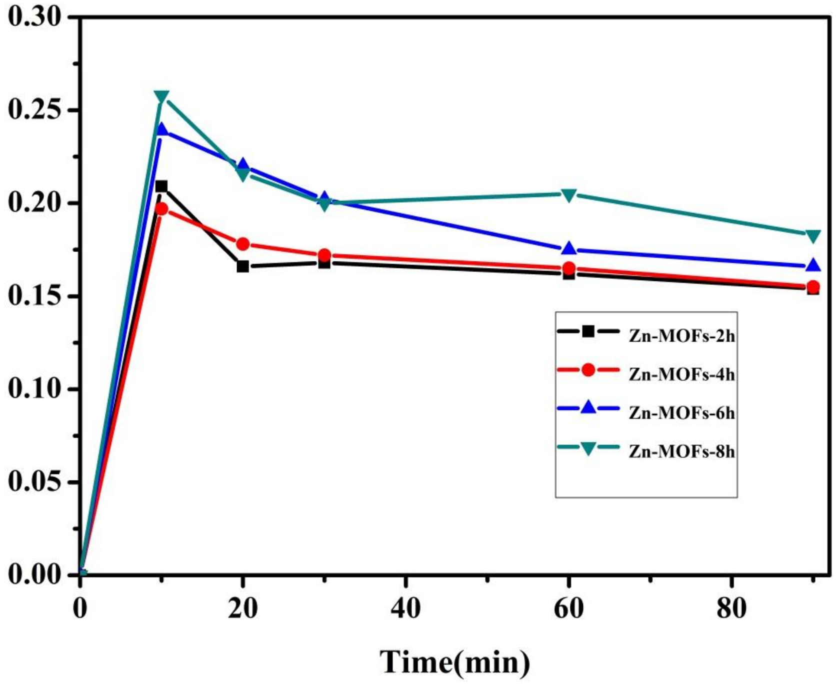

Figure S12 Changes in the amounts of super oxide anion radical species over reaction time caused by MOF/LZH-6 composite.

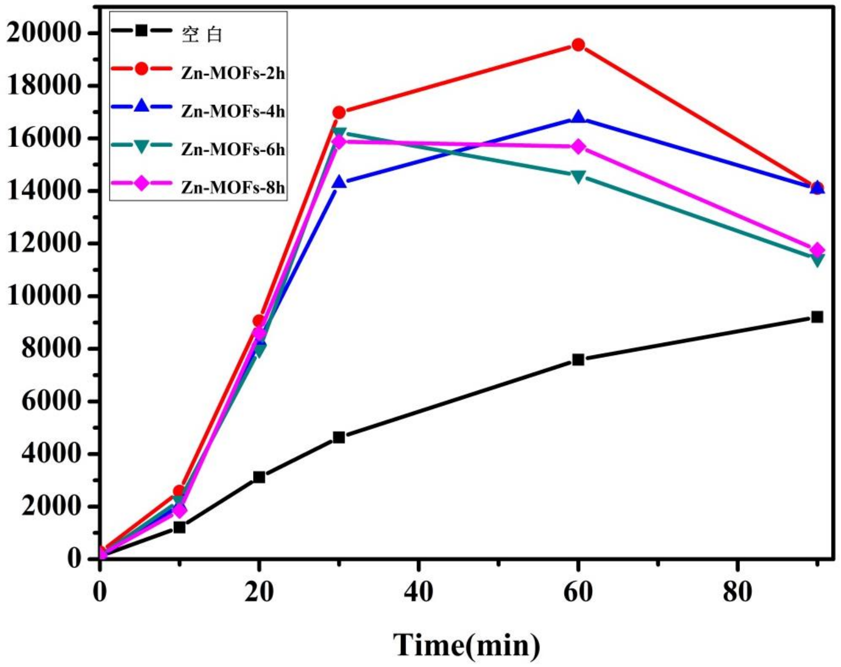

Figure S13 Changes in the amounts of OH radicals over reaction time caused by MOF/LZH-6 composite.